METHOD AND APPARATUS FOR PRODUCING AMORPHOUS ALLOY SHEET, AND AMORPHOUS ALLOY SHEET PRODUCED USING THE SAME

Technical Field

The present invention relates to a method for producing an amorphous or noncrystalline alloy, and more particularly, to a method for producing a bulk amorphous alloy sheet.

Background Art

An amorphous alloy is a material that has a liquid phase-like microstructure with no crystallinity due to disordered arrangement of atoms, and contains no crystalline imperfections such as grain boundary and dislocation, unlike a conventional crystalline alloy. Therefore, an amorphous alloy is a significantly improved material in terms of mechanical properties such as strength, magnetic properties, corrosion resistance, and the like.

Due to the above-described excellent characteristics, there have been increasing interests on amorphous alloy materials, in particular, an amorphous alloy sheet as a new material that can be used for various purposes in various industrial fields including the aero-space industry, the nuclear power equipment industry, and the defense industry. However, despite the demands in various industrial fields, there have not yet been developments on efficient and industrially applicable methods for mass-producing an amorphous alloy sheet.

As for conventional processes for producing amorphous alloys, there are die casting and permanent mold casting. However, die casting and permanent mold casting are inappropriate to mass-produce amorphous alloy sheets that can be used for various purposes, as well as are not cost effective.

A melt spinning process is another conventional method for the amorphous alloy production. However, since this process is intended for production of an amorphous alloy material in the form of an ultra-thin

strip of about 0.05 mm or less in thickness, it is not suitable for production of a bulk amorphous alloy sheet.

A strip casting process is a process that produces a metal material into a sheet form. This process has advantages such as equipment investment cost reduction, low energy consumption, and high proportion of products relative to raw materials. However, it has been understood that a conventional strip casting process is not suitable for production of an amorphous alloy sheet, and thus, no reports have been made on examples of use of a conventional strip casting process for production of an amorphous alloy sheet. Even probabilities that a conventional strip casting process may be used in production of an amorphous alloy sheet have been denied.

Therefore, in order for a bulk amorphous alloy with good properties to be used for more various purposes in more various industrial fields, development of a method for mass-producing a bulk amorphous alloy, in a sheet form with high utility, at low production cost, is required.

Disclosure of the Invention

The present invention provides a method for producing a bulk amorphous alloy sheet with high quality at low production cost, by which an alloy melt can be directly transformed into a sheet form without using other additional processes.

The present invention also provides an apparatus for producing a bulk amorphous alloy sheet with high quality at low production cost, and a bulk amorphous alloy sheet.

Brief Description of the Drawings

FIG. 1 is a diagram of a method for producing an amorphous alloy sheet according to the present invention;

FIG. 2 is a schematic view of an apparatus for producing an amorphous alloy sheet according to an embodiment of the present invention;

FIG. 3 is a diagram showing transformation of an amorphous alloy melt into a sheet form that is carried out in two rolls of the apparatus of FIG. 2;

FIG. 4 is a diagram showing adjustment of a gap between two rolls in the apparatus of FIG. 2;

FIG. 5 is a diagram showing an example of an arrangement structure of two rolls in the apparatus of FIG. 2 according to an angle defined by the horizontal and a straight line connecting the respective rotation centers of the two rolls;

FIG. 6 is an X-ray diffraction pattern of an amorphous alloy sheet produced according to Example of the present invention; and

FIG. 7 is an optical microphotograph of the microstructure of an amorphous alloy sheet produced according to Example of the present invention.

Best mode for carrying out the Invention

A method for producing an amorphous alloy sheet according to the present invention comprises: preparing a melt containing alloy components; feeding the melt into a gap defined between two rolls, which rotate in opposite direction to each other, and each of which is provided with heat exchange means; and cooling the melt at a cooling rate higher than the critical cooling rate for transformation of the melt into an amorphous solid phase when the melt passes through the gap defined between the two rolls.

An apparatus for producing an amorphous alloy sheet according to the present invention comprises: a crucible for receiving a melt containing alloy components, which is provided with a melt outlet; two rolls, each of which is provided with heat exchange means to cool the melt at a cooling rate higher than the critical cooling rate for transformation of the melt into an amorphous solid phase when the melt passes through a gap defined between the two rolls; and a connecting channel for passing the melt from the melt outlet of the crucible to the gap defined between the two rolls.

Hereinafter, a method for producing an amorphous alloy sheet according to the present invention will be described in detail. FIG. 1 schematically shows a method for producing an amorphous alloy sheet according to the present invention.

The step of preparing a melt can be carried out, for example, using a melting furnace which is provided with heating means suitable for melting alloy components and with a sealable crucible.

The heating means provided in the melting furnace can be operated in a heating manner such as resistance heating, arc heating, induction heating, infrared heating, e-beam heating, and laser heating, but is not limited thereto.

The step of preparing a melt can be carried out in an inert or non-inert atmosphere. As for some specific alloys, non-crystallization requires an inert atmosphere. In this case, it is preferable to carry out the step of preparing a melt in an inert atmosphere.

In a case where the step of preparing a melt is carried out using the aforementioned melting furnace, an inert atmosphere can be accomplished by feeding an inert gas into the melting furnace. Examples of an inert gas to be used herein include helium, neon, argon, krypton, xenon, radon, nitrogen, or a mixture thereof. Alternatively, an inert atmosphere can be accomplished by maintaining the sealable crucible in a vacuum state.

The step of preparing a melt can also be carried out in other specific atmospheres required for specific alloys. In this case, gases required for formation of such specific atmospheres are fed into the crucible.

A melt thus prepared is fed into a gap defined between the two rolls, which rotate in opposite direction to each other, and each of which is provided with heat exchange means. According to an embodiment of the present invention, the melting furnace can have a melt nozzle, which is located to be near the two rolls. The melt is fed into the gap defined between the two rolls through the melt nozzle.

The melt fed into the gap defined between the two rolls is cooled

at a cooling rate higher than the critical cooling rate for transformation of the melt into an amorphous phase. In order to accomplish such rapid cooling, the two rolls may be made of a material with good heat conductivity and may be provided with heat exchange means. A copper-based alloy material can be used as a good heat conductive material for the two rolls, but is not limited thereto. The heat exchange means to be installed in the two rolls may be, for example, a circuit for flow of a cooling fluid, but is not limited thereto. The cooling fluid may be cooling water or cooling oil.

There are no particular limitations on the diameter and rotation rate of the two rolls. However, in view of a heat transfer, a linear velocity at the circumferences of the two rolls may be in the range of about 1 to 10 cm/sec. Also, there are no particular limitations on the gap between the two rolls. However, in view of a heat transfer and/or a thickness of a desired sheet, the gap between the two rolls may be in the range of about 0.5 to 20 mm. As long as an object of the present invention can be accomplished, the gap between the two rolls may also be less than about 0.5 mm or more than about 20 mm. In addition, there are no particular limitations on the width of the rolls. The width of the rolls can be appropriately determined depending on the maximum width of a desired sheet.

Generally, the critical cooling rate for amorphous phase formation varies depending on types of alloys. An appropriate cooling rate for a specific alloy can be realized by adjusting the circulation rate of a cooling fluid, the rotation rate of the two rolls, the gap between the two rolls, the temperature of the melt, etc.

The melt is cast into an amorphous alloy sheet by the above-described rapid cooling and then removed away from the rolls. Due to rolling effect by the two rolls, generation of cracks and air gaps is prevented, which was identified by X-ray diffraction and microscope image analysis results.

In a method of the present invention, if the temperature of the melt to be fed into the gap defined between the two rolls is too low, melt

feeding is not smoothly carried out, and thus, it is difficult to produce a sheet. On the other hand, if it is too high, the melt is not sufficiently cooled even using the two rolls and the heat exchange means, and thus, it is difficult to produce an amorphous sheet.

If the surface temperature of the two rolls is too low, the melt is not cooled by a uniform proportion, and thus, the loading of the melt is not smoothly carried out. Furthermore, cracks may be caused in edges of a formed sheet. On the other hand, if it is too high, it is difficult to obtain a cooling rate above the critical cooling rate.

If the rotation rate of the two rolls is too slow, solidification of the melt may be completed before an amorphous solid alloy is completely removed away from the rolls, and thus, operation of the rolls may be suspended. On the other hand, if it is too fast, uniform cooling is not sufficiently accomplished, and thus, it is difficult to produce a sheet with high quality.

If the gap between the two rolls is too small, it is difficult to produce a bulk amorphous alloy sheet. Furthermore, due to excess feeding of the melt, other process factors may be adversely affected. At the same time, cracks may be caused in edges of a formed sheet. On the other hand, if it is too large, a sheet may be formed to an excessive thickness, and thus, a cooling rate above the critical cooling rate cannot be realized at the center portion of a sheet. As a result, it is difficult to obtain a uniform, high quality amorphous alloy.

By way of an illustrative example, in case of a copper-based amorphous alloy comprised of 45 to 49 atomic% Cu, 32-34 atomic% Ti, 10-13 atomic% Zr, 5-7 atomic% Ni, 1-3 atomic% Sn, and 0.5-2 atomic% Si, the temperature of the melt to be fed into the gap defined between the two rolls may be set to a range of about 500 to 1,500℃, the surface temperature of the two rolls a range of about 15 to 30℃, the rotation rate of the two rolls a range of about 1 to 10 cm/sec, and the gap between the two rolls a range of about 0.5 to 20 mm.

It should be understood that the method of the present invention can be applied to all types of alloys capable of being transformed into an

amorphous phase, in addition to the above copper-based alloy.

Hereinafter, an apparatus for producing an amorphous alloy sheet according to the present invention will be described in detail. The apparatus can be efficiently used in production of an amorphous alloy sheet according to the above-described method.

An apparatus for producing an amorphous alloy sheet according to the present invention comprises: a crucible for receiving a melt containing alloy components and provided with a melt outlet; two rolls, each of which is provided with heat exchange means to cool the melt at a cooling rate higher than the critical cooling rate for transformation of the melt into an amorphous solid phase when the melt passes through a gap defined between the two rolls; and a connecting channel for passing the melt from the melt outlet of the crucible to the gap defined between the two rolls.

FIG. 2 schematically shows an apparatus for producing an amorphous alloy sheet comprising a crucible 10, a connecting channel 20, and two rolls 30, according to an embodiment of the present invention.

The crucible 10 may be a melting crucible that can control an atmosphere therein. As shown in FIG. 2, the crucible 10 receives a melt containing alloy components and is provided with a melt outlet 18. The crucible 10 also comprises a gas supply unit 16 for controlling an atmosphere in the crucible 10 and a heating unit 14 for melting alloy components to prepare the melt and maintaining the temperature of the prepared melt.

The crucible 10 may further comprise a stopper 12 that can open and shut the melt outlet 18 to control the release of the melt.

The connecting channel 20 may comprise a heating unit 22 that can maintain the temperature of the melt in the connecting channel 20 while the melt flows from the crucible 10 to the gap defined between the rolls 30. The connecting channel 20 may further comprise a gas supply unit 24 that can control an atmosphere in the connecting channel 20.

The two rolls 30 may be made of a copper-based alloy containing

material. However, since there are no particular limitations on a material for the two rolls, the two rolls may also be made of other types of materials with good heat conductivity.

Each of the two rolls 30 may comprise a circuit 32 for flow of a cooling fluid as the heat exchange means. The cooling fluid may be cooling water or cooling oil.

FIG. 3 is a detailed view of the two rolls of FIG. 2 and schematically shows transformation of the melt into a solid sheet by cooling when the melt passes through the gap defined between the two rolls. An alloy melt, which can be transformed into an amorphous phase, is fed into the gap defined between the two rolls 30 in rotation, then the melt is cooled while being in contact with the two rolls 30 and cast into a solid sheet. The sheet thus obtained is removed away from the two rolls 30 by rotation of the two rolls 30. At this time, in order for the cooling rate of the melt by contact of it with the two rolls 30 to be higher than the critical cooling rate for formation of an amorphous phase, the two rolls 30 is cooled by the heat exchange means. The alloy melt is strongly pressed by the two rolls 30 to cast into an amorphous alloy sheet and then is removed away from the two rolls 30.

If the gap between the two rolls is too small, it is difficult to produce a bulk amorphous alloy sheet. Furthermore, due to excess feeding of the melt, other process factors may be adversely affected. At the same time, cracks may be formed at the edges of a formed sheet. On the other hand, if it is too large, a cooling rate above the critical cooling rate cannot be realized in a center portion of a sheet. As a result, it is difficult to obtain a uniform, high quality amorphous alloy sheet. In this regard, the gap between the two rolls 30 may be in the range of about 0.5 to 20 mm. The two rolls may be installed to be spaced apart at a predetermined distance from each other, or may be installed in such a way that the gap between the two rolls can be adjusted when needed. FIG. 4 schematically shows adjustment of a gap between the two rolls.

FIG. 5 schematically shows the structure of the two rolls arranged

in such a manner that an angle defined by the horizontal and a straight line connecting the respective rotation centers of the two rolls, is in the range of 0 to 90 degrees. The angle may vary depending on characteristics of a melt such as fluidity. For example, if the fluidity of a melt is high, the two rolls can be vertically installed (i.e., the angle is 90 degrees) to smoothly carry out horizontal supply of a melt and release of a sheet. On the other hand, if the fluidity of a melt is insufficient, the two rolls can be horizontally installed (i.e., the angle is 0 degrees) to smoothly carry out vertical supply of a melt by gravity and release of a sheet. The two rolls may be installed at a fixed angle selected from the angle of 0 to 90 degrees or may be installed in such a way that the angle can be adjusted in the range.

If the rotation rate of the two rolls is too slow, solidification of a melt may be completed before an amorphous solid alloy is completely removed away from the rolls, and thus, operation of the rolls may be suspended. On the other hand, if it is too fast, uniform cooling is not sufficiently accomplished, and thus, it is difficult to produce a sheet with high quality. In this regard, the two rolls may be installed in such a way to be operated at a rotation rate of about 1 to 10 cm/sec. To this, the two rolls may be connected to conventional driving means (not shown).

Hereinafter, a bulk amorphous alloy sheet according to the present invention will be described in detail.

A bulk amorphous alloy sheet according to the present invention is either a bulk alloy material that consists of fully amorphous phase or a bulk alloy material that consists of composite containing amorphous and crystalline phases.

The term, "bulk sheet" as used herein indicates that an amorphous alloy of the present invention is processed into a material which has structural continuity and a relatively large two- or three-dimensional dimension, not into a thin film (of 100 μm or less in thickness, for example) dimension. For example, an amorphous alloy sheet of the present invention may have a thickness of about 0.5 to 20 mm, but is not limited thereto. Also, there are no particular limitations

on the width, length, and shape of an amorphous alloy sheet of the present invention. Such a bulk amorphous alloy sheet can be used for various purposes. Also, attentions have been paid to such a bulk amorphous alloy sheet as a new material in the whole industrial fields including the nuclear power equipment industry (metal pipe), the defense industry (amorphous metal-tungsten composite penetrator), the sports equipment industry (golf clubs), and the aero-space industry.

The bulk amorphous alloy sheet according to the present invention can be produced by the above-mentioned method according to the present invention.

The bulk amorphous alloy sheet according to the present invention may consist of composite containing amorphous and crystalline phases. In that case, the volume or weight ratio of amorphous phase to crystalline phase in the composite can be controlled by varying the process conditions in the above-mentioned method according to the present invention.

The bulk amorphous alloy sheet according to the present invention may typically contain an amorphous phase of about 90% by volume or more, preferably about 96% by volume or more.

In experiments of producing an amorphous alloy sheet using the above-described method and apparatus of the present invention, amorphous alloy sheets containing an amorphous phase of at least about 96% by volume, even about 100% by volume were obtained. Typically, an amorphous alloy sheet of the present invention may contain an amorphous phase of about 96.0% by volume to about 99.9% by volume.

On the other hand, the bulk amorphous alloy sheet according to the present invention may also contain amorphous phase of about 90% by volume or less.

There are no particular limitations on alloy compositions to be used in a method and an apparatus for producing an amorphous alloy sheet of the present invention, and an amorphous alloy sheet produced by the method and apparatus. For example, there may be used

amorphous alloy compositions such as $Cu_{47}Ti_{34}Zr_{11}Ni_8$ [S. C. Glade, W. L. Johnson: J. Appl. Phys., vol.89 (2001) pp. 1573-1579]; $Cu_{47}Ti_{33}Zr_{11}Ni_8Si_1$ [M. Calin: Scripta Mater., in press (2003)]; $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$ [D. H. Bae, H.K. Lim, S.H. Kim, D.H. Kim and W.T. Kim: Acta Materialia, vol. 50 (2002) pp. 1749-1759]; $Cu_{60}Zr_{30}Ti_{10}$, $Cu_{60}Hf_{25}Ti_{15}$ [Akihisa Inoue, Wei Zhang, Tao Zhang and Kei Kurosaka: J. of Non-Crystalline Solids, vol. 304 (2002) pp. 200-209]; $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ [H. Choi-Yim, R. D. Conner, F. Szuecs and W. L. Johnson: Acta Materialia, vol. 50 (2002) pp. 2737-2745]; $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ [J. Schroers, R. Busch, S. Bossuyt and W. L. Johnson: Mater. Sci. & Eng. A., vol. 304-306 (2001) pp. 287-291]; and $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ [M. Sherif El-Eskandarany, J. Saida and A. Inoue: Acta Materialia, vol. 51 (2003) pp. 4519-4532].

Hereinafter, the present invention will be described more specifically by Example. However, the following Example is provided only for illustration and thus the present invention is not limited thereto.

<Example>

In this Example, a copper-based alloy with its chemical composition presented in Table 1 was used as a mother alloy. An apparatus shown in FIG. 2 was used.

Table 1

Chemical composition of mother alloy

Elements	Cu	Ti	Zr	Ni	Sn	Si
Content (atomic%)	47	33	11	6	2	1

3 kg of a copper-based mother alloy was loaded into a high purity graphite crucible and then maintained at a temperature of about 1,400℃ for about 60 minutes to be completely melted into a liquid phase. A copper-based mother alloy melt thus obtained was discharged while being maintained at a temperature of about 1,200℃, and then transferred into an inlet between rolling rolls of the strip casing

apparatus.

The rotation rate, surface temperature, and gap of the rolling rolls were about 2.0 cm/sec, about 20℃, and about 2 mm, respectively. Under these process conditions, amorphous alloy sheets of 1 m in length, 10 cm in width, and 2 mm in thickness were prepared.

The non-crystallinity of the copper-based amorphous alloy sheets thus prepared was determined by X-ray diffraction analysis and the result is presented in FIG. 6. As shown in FIG. 6, the amorphous alloy sheets obtained in Example were in an amorphous phase that contained the small volume fraction of a crystalline phase.

The cross-sections of the copper-based amorphous alloy sheets obtained in Example were subjected to an optical microscope image analysis and the resultant cross-sectional microphotograph is presented in FIG. 7. As shown in FIG. 7, no air gaps or cracks that may be caused by solidification and contraction of a melt were observed in the alloy sheets obtained in Example. In addition, the amount of an amorphous phase in the amorphous alloy sheets was evaluated. According to the evaluation result, the alloy sheets obtained in Example contained an amorphous phase of about 96% by volume or more. Therefore, it was demonstrated that the alloy sheets obtained in Example are excellent amorphous alloy sheets.

Industrial Applicability

As apparent from the above descriptions, a method and an apparatus for producing an amorphous alloy sheet according to the present invention is used in production of an amorphous alloy sheet of high quality, in which the generation of air gaps and cracks is remarkably reduced.

According to a method and an apparatus for producing an amorphous alloy sheet of the present invention, an amorphous alloy sheet can be directly prepared from a melt without using a separate process. Therefore, the amorphous alloy sheet, which has very high industrial applicability, can be produced in large scale and at very low

cost. Consequently, the application range of an amorphous alloy can be economically extended.